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Orbital valency force field constants and ionicity of M—X bond of tetrahalides of IV group elements

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Orbital valency force field constants are evaluated utilising the recent vapour phase vibrational spectral data for some IV group tetrahalides. The results are discussed in the light of ionicity of M–X bond and bond stretching force constants for fluoro species of Si and Fe have been predicted.

1. INTRODUCTION

The vapour phase vibrational spectra of IV group tetrahalides have been reported by Clark *et al* (1971, 1972). A fresh evaluation of potential constants was thought necessary since earlier workers used crystal frequencies in their evaluation of force constants. A few molecules among these systems have been subjected to GVFF study but the frequency data used were inaccurate as compaired to the existing ones. Further, it is interesting to interpret the results in the light of force constants ionicity relation proposed by Yeranose (1969).

2. OVFF AND IONICITY OF M–X BOND

Electronegativity difference between M and X atoms has a linear relationship with the force constant. This difference is defined as *Ioncity* by Yeranose (1969). This ionicity of M–X chemical bond may be represented by

$$\omega = 16(x_M - x_X) + 3{\cdot}5(x_X - x_X)^2 + \theta_f$$

where x_M and x_X are electronegativities of the metal and halogen atoms respectively, and θ_f is a constant which assumes different values for different molecular systems.

The method used for the evaluation of OVFF constants is the same as those used in our earlier communications (Sanyal *et al* 1969, 1970).

k_1 the bond stretching force constant, k_α the inter-bond angle distortion constant, the interaction constant between non-bonded atoms (A and B/R) were calculated with the help of four equations (Heath & Linnett 1948), using four fundamental frequencies given in table 1, without assuming any relationship between A and B/R. The OVFF constants, thus calculated are shown in table 2.

Table 1. Fundamental frequencies of the tetrahalides of group IV elements

Molecule	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
CF_4	908.4	434.4	1283.0	631.2
SiF_4	800.8	264.2	1029.6	388.7
CCl_4	460.0	214.2	792/765	313.5
$SiCl_4$	423.1	145.2	616.5	220.3
$GeCl_4$	396.1	125.0	459.0	171.0
$SnCl_4$	396.1	95.2	408.2	126.1
$SiBr_4$	246.7	84.8	494.0	133.6
$GeBr_4$	235.7	74.7	332.0	111.1
$SnBr_4$	222.1	59.5	284.0	85.9
SiI_4	166.3	57 6	405.6	90.0
GeI_4	156.0	51.6	273.0	77.3
SnI_4	147.7	42.4	210.4	63.0

Table 2. Calculated values of OVFF constants using four equations and OVF constants using Lennard-Jones potential $A = 6{\cdot}5\ B/R$ (mdyn/A)

Molecule	Field	k_r	k'	A	B/R
CF_4	OVFF	5.288	1.255	0.495	−0 110
	$A = 6{\cdot}5\ B/R$	(4 591)	(0 882)	(0 580)	(0 089)
SiF_4	OVFF	5.807	0.345	0.171	0.094
	$A = 6{\cdot}5\ B/R$	(5.809)	(0.345)	(0.143)	(0.022)
CCl_4	OVFF	1.090	0.268	0.314	0.062
	$A = 6{\cdot}5\ B/R$	(1.966)	(0.298)	(0.306)	(0 047)
$SiCl_4$	OVFF	2.654	0.119	0.135	0.050
	$A = 6{\cdot}5\ B/R$	(2.758)	(0.214)	(0.122)	(0.018)
$GeCl_4$	OVFF	2.513	0.101	0.096	0.034
	$A = 6{\cdot}5\ B/R$	(2.571)	(0.136)	(0.088)	(0.013)
$SnCl_4$	OVFF	2.465	0.093	0.049	0.022
	$A = 6{\cdot}5\ B/R$	(2.464)	(0.086)	(0.047)	(0.007)
$SiBr_4$	OVFF	2.194	0.151	0.084	0.020
	$A = 6{\cdot}5\ B/R$	(2.194)	(0.157)	(0.083)	(0.013)
$GeBr_4$	OVFF	2.318	0.274	0.037	−0.086
	$A = 6{\cdot}5\ B/R$	(1.999)	(0.097)	(0.077)	(0.011)
$SnBr_4$	OVFF	2.003	0.111	0.040	−0.024
	$A = 6{\cdot}5\ B/R$	(1.905)	(0.053)	(0.052)	(0.008)
SiI_4	OVFF	1.593	0.135	0.059	0.006
	$A = 6{\cdot}5\ B/R$	(1.528)	(0.102)	(0.067)	(0.010)
GeI_4	OVFF	1.507	0.112	0.039	0.010
	$A = 6{\cdot}5\ B/R$	(1.524)	(0.119)	(0.036)	(0.005)
SnI_4	OVFF	1 279	0.032	0.044	0.014
	$A = 6{\cdot}5\ B/R$	(1.305)	(0.046)	(0.040)	(0.006)

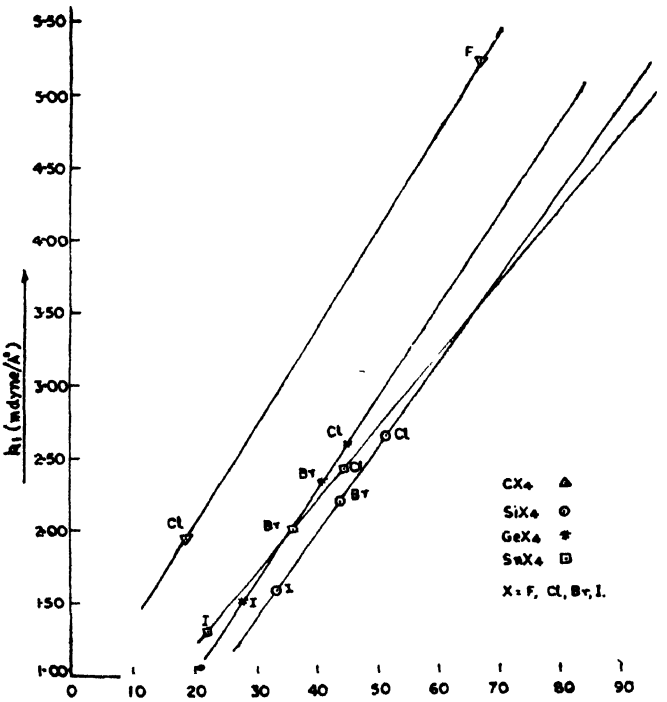
As it is seen from table 2, the present calculation leads to negative values of B/R in certain cases. Negative sign, itself has no physical significance and it shows that OVFF in some cases cannot represent the actual interaction between the non-bonded atoms satisfactorily by the single term B/R.

3. Results and Discussion

The force constants of CCl_4, $SiCl_4$, $GeCl_4$ and $SnCl_4$ indicate certain regularities. Where the stretching constant (K_1 for all molecules (except CCl_4) from Si to Sn decreases with the increase in the mass of the central atom. Similar decrease of bond strength is also seen in this group. The low value of the bond stretching force constant K_1 for CCl_4 (1.909 mdyne/Å) indicates small stretching, due to repulsion between the non-bonded atoms.

On approximating the interaction by the Lennard-Jones potential (i.e., using $A = 6{\cdot}5\ B/R$), we obtain another set of force constants shown in parenthesis (table 2).

The relation between K_1 and w for tetrahalides of C, Si, Ge and Sn is shown in figure 1. Extrapolated values of u_1 for SiF_4 and GeF_4 are 5·87 mdyne/Å



VARIATION OF BOND STRETHING FORCE CONSTANT k_1 WITH IONICITY ω.

Fig. 1.

and 5·78 mdyne/Å respectively. The bond stretching force constant varies linearly with the ionicity w as shown in the figure. The slope of the curves decreases with increase in the principal quantum number n of the central atom of the series.

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